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Method of Forming Non-sag Molybdenum-Lanthana Alloys

5 TECHNICAL FIELD

This invention relates generally to methods for forming dispersion-strengthened alloys of molybdenum. More particularly, this invention relates to methods of forming molybdenum-lanthana alloys having non-sag microstructures.

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BACKGROUND OF THE INVENTION

Molybdenum alloys which have been dispersion-strengthened with particles of lanthanum oxide (lanthana), La_2O_3 , are desirable for use in high temperature applications because of their high melting point and good mechanical properties at high temperatures, in particular, resistance to sag and creep. The alloys are formed by combining molybdenum powder with from about 0.1 to about 5 weight percent (wt.%) of lanthanum oxide powder or an equivalent amount of a lanthanum oxide precursor, such as $\text{La}(\text{OH})_3$ or $\text{La}(\text{NO}_3)_3$, which is then converted to the oxide by heating. The size of the lanthanum oxide particles dispersed in the molybdenum matrix is generally preferred to be less than about 1 μm , however, the particles may be as large 5-10 μm . After compacting and sintering, the sintered body is deformed by mechanical working, e.g., rolling, swaging, drawing, or hammering, and then is then recrystallized to generate the desired microstructure. For sag and creep resistance, the preferred microstructure consists of large, interlocking grains which are elongated in the direction of the applied mechanical work.

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The recrystallization behavior of the alloy is affected by the prior amount of deformation. When the undeformed or fully recrystallized alloy is being cold worked, the density of dislocations within the alloy increases. This occurs first at the grain boundaries and then progresses further into the bulk of the grains as the amount of cold work increases. Prior art methods have employed high degrees of deformation (>60%) in order to achieve high-temperature strength and creep-resistance.

Japanese Patent Publication 59-177345 (1984) describes a molybdenum-lanthana alloy for structural purposes. The alloy has a high secondary recrystallization temperature and high high-temperature strength. The alloy contains 1 to 5 wt.% lanthana (La_2O_3) particles having an average size of not more than 3 μm which are uniformly dispersed in molybdenum. For structural purposes, the material is preferably worked from the sinter by a working factor of at least 60% and then heated above the secondary recrystallization temperature.

U.S. Patent No. 4,950,327 to Eck et al. (1990) describes a high-temperature, creep-resistant molybdenum-lanthana alloy having a tiered structural arrangement. After sintering, the alloy is mechanically reformed in gradations of about 10% without heating the alloy above its recrystallization temperature. Once the degree of reforming is at least 85%, the alloy is finally subjected to a recrystallization anneal.

One disadvantage with the prior art methods is that the dimensions of the feed material must be substantially greater than the dimensions of the finally recrystallized material in order to impart the required high degree of deformation. This

leads to less flexibility in the manufacturing process. Another disadvantage is that the large amount of stored energy in the material caused by the high degree of deformation can lead to spontaneous grain growth in the material during recrystallization. This may make it more difficult to control grain size in the finally recrystallized material.

SUMMARY OF THE INVENTION

It has been discovered that a non-sag microstructure can be obtained in a molybdenum-lanthana alloy using a degree of deformation of from about 7% to about 18%. As used herein, the degree of deformation refers to the percentage reduction in at least one dimension of the feed material, e.g., sheet thickness. Preferably, the degree of deformation is from about 12% to about 17%. The alloy may be deformed directly from the as-sintered state to its finished form and then finally recrystallized or, preferably, the alloy can be worked from the as-sintered state to a near-finished form, recrystallized, and then deformed to its finished form and finally recrystallized. Preferably, the recrystallization of the alloy in its near-finished form is conducted at a temperature of from about 1150°C to about 1400°C. The final recrystallization is preferably conducted at about 1900°C. Preferably, the amount of lanthana in the alloy ranges from 0.4 wt.% to about 1.0 wt.%, more preferably, from about 0.6 wt.% to about 0.7 wt.%.

The grain size after final recrystallization is larger because the predominant mechanism occurring during the heat treatment is the annihilation of dislocations at the neighboring grain boundaries causing some grain boundaries to disappear. This is generally referred to as strain-induced grain boundary migration. After final recrystallization, the grains tend to

exhibit less elongation than grains resulting from methods which use high degrees of deformation. Typically, the aspect ratio for the grains produced by the method of this invention is no more than 4:1. Also, since the degree of reformation needed to produce the non-sag microstructure is about 18% or less, the feed material need not be much larger than the finished product and there is a greater potential to control grain size in the finished material because of the lower amount of stored energy in the material prior to final recrystallization. Hence, the method of this invention is more flexible for manufacturers of refractory metal products.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1A is a photomicrograph of the microstructure of the molybdenum-lanthana alloy of Example 1 after recrystallization and rolling to 0.15 cm thickness.

Fig. 1B is a photomicrograph of non-sag microstructure of the molybdenum-lanthana alloy of Example 1 after final recrystallization.

Fig. 2A is a photomicrograph of the microstructure of the molybdenum-lanthana alloy of Example 2 after recrystallization and rolling to 0.10 cm thickness.

Fig. 2B is a photomicrograph of non-sag microstructure of the molybdenum-lanthana alloy of Example 2 after final recrystallization.

DETAILED DESCRIPTION OF THE INVENTION

For a better understanding of the present invention, together with other and further objects, advantages and capabilities

thereof, reference is made to the following disclosure and appended claims taken in conjunction with the above-described drawings.

EXAMPLE 1

Pure molybdenum metal powder with grain size of $3.5\text{ }\mu\text{m}$ was mixed with 0.7 weight percent (wt.%) of $\text{La}(\text{OH})_3$ powder having a grain size of $0.65\text{ }\mu\text{m}$. The mixture was isostatically pressed at 240 MPa to form a pressed slab with dimensions of 64 cm x 38 cm x 5 cm. The slab was subsequently rolled at varying temperatures; starting at 980°C , followed by 785°C , and finally at ambient temperature to a thickness of 0.17 cm. The sheet was then recrystallized at 1400°C and then rolled at ambient temperature to the thickness of 0.15 cm, (about 12% deformation). The microstructure of the recrystallized and rolled sheet is shown in Fig. 1A. The rolled sheet was subjected to a final recrystallization anneal at 1900°C to produce the non-sag microstructure which is shown in Fig. 1B.

Example 2

Pure molybdenum metal powder with grain size of $3.5\text{ }\mu\text{m}$ was mixed with 0.7 wt.% $\text{La}(\text{OH})_3$ powder with a grain size of $0.65\text{ }\mu\text{m}$. The mixture was isostatically pressed at 240 MPa to form a pressed slab with dimensions of 64 cm x 38 cm x 5 cm. The slab was subsequently rolled at varying temperatures; starting at 980°C , followed by 785°C , and finally at ambient temperature to a thickness of 0.12 cm. The sheet was then recrystallized at 1150°C . Subsequently it was rolled at ambient temperature to the

thickness of 0.10 cm (about 17% deformation). The microstructure of the recrystallized and rolled sheet is shown in Fig. 2A. Upon a final recrystallization anneal at 1900°C, the sheet material exhibited the non-sag microstructure shown in Fig. 2B.

The sag resistance of 0.5 in. x 5.6 in. samples of the non-sag molybdenum-lanthana sheet material from Examples 1 and 2 was measured according to the following procedure. The samples were supported at opposite ends and a 10 g weight placed on the sample at the center point between the supports. The distance between the supports was 4.2 inches. At the start of the test, the distance between the reference plate and the 0.15-cm-thick sample was 0.5 in. at the point directly below the 10-g load. The corresponding distance for the 0.10-cm-thick sample was 0.4375 in. at the start of the test. Sag was measured as the amount of deflection of the sample toward the reference plate after heating the sample at 1900°C for 1 hour. Six such heating cycles were carried out for each sample and the amount of deflection measured after each cycle. The cumulative amount of deflection is reported in the following table. The sag resistance of the materials was found to be equivalent to commercially available non-sag molybdenum-lanthana sheet material.

Table

Material Thickness	Width (in.)	Length (in.)	Center Load (g)	Total Sag (in.)
0.15 cm	0.5	5.6	9.99	0.0625
0.10 cm	0.5	5.6	9.98	0.0313

While there has been shown and described what are at the present considered the preferred embodiments of the invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the scope of the invention as defined by the appended claims.